College Chemistry 1

* الكتاب: College Chemistry 1

* الكاتب: د.محمد عبدالفتاح ابراهيم

* مراجعة لغوية: قسم التحرير والمراجعة بدار المنتدى

* تصميم الغلاف: قسم الجرافيك بدار المنتدى

* إخراج داخلي: القسم الفني بدار المنتدى

* رقم الإيداع: 20660/ 2022

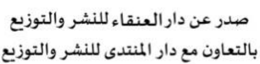
* الترقيم الدولي: 978-977-86274-6-6

المدير العام: الأستاذ عزيز عثمان



















College Chemistry 1

Edited by

Dr. Mohamed Abdelfattah Ibrahim

Faculty of Science

El-Arish University





To my wife Sohir and my daughters Soha and Aliaa



Preface

In this book I tried to collect all physical chemistry experiments in college level.

This book is very important and valuable for students of faculty of science, pharmacy, medicine, and medical science. They can use it as lab manual book.



Chapter 1

Safety Roles



Hazard Classes

- Hazardous chemicals will display one or more of the following characteristics:
  - Flammable
  - Reactive
  - Toxic
- They may also present unique danger

1- Flammability / Explosive Risk

- Some chemicals present a fire or explosion hazard.
- These materials may be present in your lab in the form of a solid, liquid, or gas.

- Sources of ignition must be controlled or eliminated when working with flammable or explosive materials.
- Appropriate PPE can reduce injury in the event of a fire.

2- Flammability / Explosive Risk



- Lab personnel should receive fire safety training.
- Training should include information on:
  a- Communication (9-1-1)
  b- Egress and evacuation
  c- Use of fire extinguishers

3- Reactivity

- Some chemicals react violently when exposed to other materials.
- "Other materials" might include lab chemicals, but may also include wood, plastic, or metal furnishings.
- Some chemicals react on contact with air and/or water.
- Energy is released rapidly and often unexpectedly.
- Oxidizers are an important type of reactive material.
- Oxidizers are frequently corrosive.
- It is important to separate oxidizers from organics.
- Special reactive materials are discussed later.

4- Toxicity

- Toxic substances cause injury to the body when we are exposed to them.
- The severity of injury or illness is dependent on a number of factors, but the most important factor is the dose.

- Dose is proportional to the amount of chemical in the environment and the duration of exposure.
- The toxic effects of many chemicals are not well characterized.
- Carcinogens frequently do not have a “safe” level of exposure.

5- Communication of Hazards

- Lab managers must ensure hazards are communicated to their personnel.
- Employees have a “right to know” the hazards in their work place.
- Communication takes many forms:
  - a- Formal classroom training
  - b- Hands-on training inside the lab
  - c- Continuous informal conversations
  - d- MSDS’s, signage, and labels

6- Inhalation Hazards

- Inhalation (breathing) hazards consist of gases, vapors, and aerosols.
- Cylinders of toxic gas should be stored in ventilated gas cabinets.
- Even “inert” gases can displace oxygen and cause asphyxiation.

- Vapors start as liquids but readily evaporate and act like gases.

8- Skin Absorption



- Certain chemicals may be absorbed through your skin.
- Gloves and protective clothing are needed to prevent contact with these chemicals.
- Skin irritation can also be caused by contact with chemicals.

9- Punctures

- Sharps can puncture the skin.
- Broken glassware, pipettes, and syringes are examples of sharps
- Contaminated sharps can deliver a chemical into the body.
- Use sharps containers to reduce exposure

10- Hierarchy of Controls

- No matter the material, there should be controls to reduce the hazard to workers.
- These controls should be implemented based on their effectiveness and their feasibility.
- There is usually a trade-off between effectiveness and feasibility.
- When grouped in order of decreasing effectiveness, this list is known as the "hierarchy of controls".



Chapter 2

Kinetic Chemistry

Catalytic Decomposition of Hydrogen peroxide

Inhibitor-free hydrogen peroxide solutions decompose spontaneously liberating oxygen in accordance with:

$$H_2O_2 \rightarrow H_2O + 1/2\ O_2$$

The decomposition rate is markedly accelerated by solids such as manganese dioxide or $K_2Cr_2O_2$ colloidal platinum, which act as catalysts. The course of reaction may be followed either by titrating the peroxide with potassium permanganate in acid medium, or by collecting the oxygen gas evolved.

Procedure:

1- Prepare 500 ml 0.1 N of each of $KMnO_4$ H_2O_2, 100 ml acidic $K_2Cr_2O_2$ solutions (2g solid $K_2Cr_2O_2$, 20 ml 0.1 N HCl then complete with water).

2- Prepare and thermostat the following mixtures at 25 °C.

Solutions	(1)	(2)	(3)
0.1 N H_2O_2	95	95	95
H_2O	4	3	2

3- Starting with mixture 1 add 1 ml acidic $K_2Cr_2O_7$ solution and report the time of starting the decomposition (time of addition) and shake.

4- Three minutes after the start, remove 10 ml of the mixture, run it into 250 ml conical flask, containing 26 ml 2N H_2SO_4. Titrate against N/10 $KMnO_4$ solution.

5- Repeat step 4 at suitable intervals say (6, 10, 15, 20, …minutes).

6- Repeat the above steps with mixtures 2 and 3, using 2 and ml acidic $K_2Cr_2O_7$ solution, respectively.

7- Pipette 9.5 ml H_2O_2 + 0.5 ml H_2O in a conical flask, containing about 20 ml 2N H_2SO_4. Titrate the mixture against the N/10 $KMnO_4$ solution. In this case, the volume of $KMnO_4$, solution corresponds to the initial concentration of H_2O_2, a (in m/s).

Calculations:

1- The volume of $KMnO_4$ obtained at any time t, corresponds to (a-x).

2- Plot log (a-x) against t, and calculate rate constant k from the slopes of the obtained straight lines. The slope is equal to: slope = k/2.303.

3- A plot of log k against, T enables the calculation of E_a from the slope of the straight line produced using

Arrhenius equation: $k = A.\ e^{-Ea/RT}$, A is a constant and k is the rate constant.

$$Slope = -\ E_a/2.303\ R$$

4- Determine the half-life time for each mixture.

5- Calculate the thermodynamic parameters of the activated complex, $\Delta S^{\#}$, $\Delta H^{\#}$ and $\Delta G^{\#}$ for the catalytic decomposition of H_2O_2 by $K_2Cr_2O_7$ solution. Using the following equations:

$$\Delta H^{\#} = E_a - RT \quad (1)$$

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \quad (2)$$

$$\Delta S\# = -\ \frac{R^2T}{E_a}(\log k)_1 / \log (k`T/h) \quad (3)$$

where:

k: The rate constant at definite temperature

k`: Boltzman constant = 1.38×10^{-16}.

h: Planks constant = 6.62×10^{-27} erg. sec

R: Universal gas constant = 1.987 (~2) cal. K^{-1} mol^{-1}.

T: Absolute temperature

Apply equations 1, 2 and 3 at 25 °C for the calculation of $\Delta S^{\#}$, $\Delta H^{\#}$ and $\Delta G^{\#}$, respectively for mixture 2.

(1) **(2)**

Time	V_{KMnO4}	a/(a-x)	Log a/(a-x)	Time	V_{KMnO4}	a/(a-x)	Log a/(a-x)

(3)

Time	V_{KMnO4}	a/(a-x)	Log a/(a-x)	Time	V_{KMnO4}	a/(a-x)	Log a/(a-x)

(2) at 10 °C

Time	V_{KMnO4}	a/(a-x)	Log a/(a-x)	Time	V_{KMnO4}	a/(a-x)	Log a/(a-x)

(2) at 15 °C

Time	V_{KMnO4}	a/(a-x)	Log a/(a-x)	Time	V_{KMnO4}	a/(a-x)	Log a/(a-x)

R	1/T	k	Log k

For mixture (2) at 25 °C

Cal. mol^{-1}

$\Delta S^{\#}$

$\Delta H^{\#}$

$\Delta G^{\#}$

Catalystic Salt Effect

Bronsted-Bjerrum hypothesis concerning the effect of salt addition on reaction rates in examined. According to the authors, reactions between bons are assumed to proceed through the formation of an intermediate complex which decomposes unimolecularly to give the products. A reaction between the ions A and B of charges Z_A ad Z_B may be represented as:

$$A^{ZA} + B^{ZB} \rightleftharpoons X^{ZA + ZB} \rightarrow \text{Products}$$

Using a simple limiting form of the Debye-Huckel equation, Bronsted and Bjerrum derived the relation:

$$\text{Log K} = \text{constant} + Z_A Z_B \sqrt{U}$$

where K is the reaction rate constant and U the ionic strength of the reaction medium. The relation indicates that the primary effect of adding a neutral salt the action involving ions of similar charges is to accelerate it, Z_A, Z_B will be positive, whereas a reaction involving ions of opposite charges is retarded with the persulphate-iodide reaction.

$$S_2O_8^{--} + 2I^- = 2SO_4^{--} + I_2$$

An accelerating effect would be expected since ions of similar charges are involved. The reaction rate may be followed in media of different ionic strength using sodium-chloride as an indifferent electrolyte.

Experiment:

Investigation of the catalytic effect of sodium chloride on the rate constant C the perculpholis iodide reaction

Procedure:

1. Prepare 250 ml of exactly 0.04 N of each of potassium persulphate and potassium iodide, 250 ml of 0.01 N sodium thiosulphate. Standardize the thiosulphate against the persulphate (10 ml $K_2S_2O_8$ + about one gram KI + 5 ml dilute HCl, then titrate the liberated iodine with the thiosulphate).
2. The reaction is followed in each of the following five mixtures in turn.

Mixture composition	1	2	3	4	5
ml distilled water	50	40	30	20	10
ml 4 N NaCl	-	10	20	30	40
ml 0.04 N KI	25	25	25	25	25
ml 0.04 N $K_2S_2O_8$	25	25	25	25	25

Each mixture is then 0.01 N with respect to each of $S_2O_8^{--}$ and I^-.

3. Starting will mixture 1, in a clean dry flask mix up the solutions in the given and the moment the last solution is

added is recorded as the starting time. stopper the flask and thermostat at 25 °C. After about 30 min and ml mixture are transferred into a flask and liberate iodine is titrated with thiosulphate using starch as indicator. Repeat with another 25 ml portion after a longer period of 50-60 min.

4. Proceed in exactly the same way with each of the other mixture.

N.B.: Skilful unipulation produce much the time needed for the experiment.

Calculations:

1. Since the normality of $S_2O_8^{--}$ and I^- in the mixture is the same as that of the thiosulphate used, namely 0.01 and 25 ml portions of mixture were , the original concentration of each of $S_2O_8^{--}$ and I^- may be taken as equal valent to 25 ml thiosulphate. If the thiosulphate titre after a time t min is x ml, the remaining concentration of each reactant is then equivalent to (25 x) ml thiosulphate. Substituting in the simplified second order equation.

$$K = \frac{1}{t}.\frac{x}{0.01(25-x)}$$

The rate constant K expressed as 1 gm equivalent min^{-1} is calculated. The mean of the two values in each mixture is then obtained.

2. Calculate the ionic strength U of each mixture from the relation $U = 1/2\sum mz$, where m and z are respectively molarity and valency of each ionic species in the reaction medium.
3. Tabulate the results for each mixture in the following order:

$$t, x, K, \text{mean } K, \log K, U, \sqrt{U}$$

4. Plot log K against $\sqrt{U}$ and comment on the results.

Clock Reactions

A slow reaction is sometimes followed by a much rapid one which however, does not occur except when the first is complete. The time elapsed from the start of reaction until the second reaction occurs in termed induction or incubation period. As an example, is the interesting reaction of II. Landolt in which sulphite is oxidized by iodate in acid medium. The first slow reaction is:

$$3H_2SO_3 + HIO_3 = 3H_2SO_4 + HI$$

When all sulphite has been oxidized to sulphate, the hydroiodic acid produced reacts immediately with iodic acid in accordance with:

$$5HI + HIO_3 = 3I_2 + 3H_2O$$

Consequently, it starch is present it the reacting mixture a dark violet colour suddenly develop at the end of the first slow reaction.

Experiment:

Determination of the rate constant and order of the sulphite-iodate reaction.

Procedure:

1. An acid sulphite solution is prepared as follows; about 2g starch are mixed thoroughly with 10 ml water, and the

suspension is added dropwise to about 10 ml boiling water. Cool, and transfer into a 250 ml measuring flask containing about 25 ml water to which 1 ml concentrated sulphuric acid is added. Accurately weighed 0.315g sodium sulphite are dissolved in the least amount of water, then carefully introduced into the flask which is then completed to the mark with distilled water, prepare also 100 ml of exactly 0.02M potassium iodate solution.

2. In dry small flat bottom flasks make up the following two series of sulphite concentrations.

Series 1		Series 2	
ml sulphate	ml water	ml sulphate	ml water
25	70	25	68
20	75	20	73
15	80	15	78
10	85	10	83

The volume of each mixture of series, 1 is then 95 ml, of series 2 is 93 ml.

3. To each mixture of series 1 in turn add exactly 5 ml iodate making a total volume of 100 ml, mix thoroughly and mean while start a clock on. Determine the induction period indiented by the sudden appearance of the blue colour.

4. To each mixture of series 2 in turn add exactly, 7 ml iodate making a total volume of 100 ml; proceed then in the same way as in step (3).

Calculations:

1. For a constant iodate concentrations, the rate equation may be written is:

$$Rate = R = KC^n,$$

where K is the rate constant, C sulphite concentration in mixture expressed is gram mole per litre, and n the order of reaction with respect to sulphite.

2. From the fact that all sulphite should have been consumed at the moment the blue colour appears, the average rate R is calculated from, R = C/t, C is sulphite concentration and t the induction period.
3. Plot log R against log C for each series of mixtures, and from the slope of the line obtained find out the order of reaction n. From the intercept, using the relation.

$$Log\ R = \log K + n \log C,$$

Calculate the rate constant K.

Determination of the order of the reaction between H_2O_2 and Hl

The reaction between H_2O_2 and HI is represented by the equation:

$$H_2O_2 + HI \rightarrow 2H_2O + I_2$$

The rate equation of this reaction is:

$$Rate = K [H_2O_2]^m [HI]^n$$

where k is rate constant, m and n are the order with respect to H_2O_2 and HI respectively.

The rate of this reaction can be determined by allowing the reaction to proceed in the presence of a small amount of thiosulphate and determining the time taken between mixing of the reactants and the appearance of iodine. The recipracol of this time interval in a measure of the rate of the reaction.

Materials:

500 ml N H_2SO_4
250 ml 0.1M KI
100 ml 0.01N $Na_2S_2O_3$
50 ml 1.0 vol H_2O_2

Procedure:

To get the order with respect to H_2O_2:

1. In dry small flat bottom flasks make up the following series of mixtures:

	I	II	III	IV	V
ml NH_2SO_4	25	25	25	25	25
ml 0.1N KI	25	25	25	25	25
ml 0.01N $Na_2S_2O_3$. $5H_2O$	5	5	5	5	5
Starch + distilled water solution	4	3	2	1	-

2. To each mixture and respectively and reparately 1, 2, 3, 4, & 5 ml 1 vol H_2O_2 (making total volume 60 ml), mix thoroughly and meanwhile start a clock on. Determine the period "t" seconds indicated by the sudden appearance of the colour. The results are tabulated as follows:

   V ml H_2O_2, t sec., 1/t, log 1/t, log VH_2O_2

3. According to the equation:

   $$\text{Log } 1/t = \log k + m \log V_{H2O2}$$

   Plot log 1/t against log V_{H2O2}. This gives a straight line, the slope of which is "m" and the intercept is log k.

To get the order with respect to KI:

1- In dry small flasks make up the following series of mixtures:

	I	II	III	IV	V
ml NH_2SO_4	25	25	25	25	25
ml 0.1N $Na_2S_2O_3.5H_2O$	5	5	5	5	5
ml 1N vol H_2O_2	2	2	2	2	2
Starch + distilled water	23	18	13	8	3

2- To each mixture add reparately and respectively 5, 10, 15, 20, 25 ml 0.1M KI solution making the total volume up to 60 ml. Start a clock and mix thoroughly. Determine the time period between addition of KI and the appearance of blue colour.

3- Tabulate the results as follows: V of KI, t, 1/t, log 1/t and log V_{KI}

4- Plot 1/t against log V_{KI}. This gives a straight line, the slope of the line is n and the intercept is log K.



Chapter 3

Surface Chemistry

(A) Surface Chemistry

Adsorption by Solids from Solution

At the surface of a solid or liquid molecular forces are usually unbalanced or unsaturated. As a result of this unsaturation exposed surfaces tend to satisfy their residual forces by attracting and retaining onto other substances with which they come in contact. The phenomenon is known as adsorption.

Solids may adsorb dissolved substances from solutions, as well as gases. In sugar refining for example, coloured materials and impurities may be removed by filtering through adsorbents such as charcoal. Adsorption of solutes from solution involves the establishment of an equilibrium between the amount adsorbed and the concentration of substance in solution. The variation of the amount adsorbed with concentration may be represented by an isotherm of the Freundlich type, viz.,

$$\frac{x}{m} = k\, C^n$$

where x is the amount of solute adsorbed per mg adsorber, C the equilibrium concentration of the solute in solution, k and n are constants. The relation may be written in the form.

$$\log \frac{x}{m} = n \log C + \log k$$

A plot of log $\frac{x}{m}$ against log C should therefore be a striahgt line of a slope n and intercept log k.

Experiment:

Determination of the adsorption isotherm of oxalic acid on bone charcoal.

Procedure:

1. Prepare 500 ml of = 0.1N $KMnO_4$, 500 ml 0.5N oxalic acid. standardize the permanganate against the acid.
2. into four small flasks introduce the following solutions:

   100 ml acid

   75 ml acid + 25 ml water

   50 ml acid + 50 ml water

   25 ml acid + 75 ml water
3. To each solution a known weight of bone charcoal (about 1g) is added. Leave for about 30 min with occasional shaking.
4. filter each solution through a dry small filter paper into a dry receiver, rejecting the few mis of filterate.
5. Titrate 10 ml filterate with permanganate

Calculations:

1. Tabulate the results as follows:

   ml $KMnO_4$ = 10 ml acid before adsorption.

ml $KMnO_4$ = 10 ml acid after adsorption.

ml $KMnO_4$ = acid adsorbed.

2. Plot x/m against C, and log x/m against log C.
3. From the latter curve find out the value of each of the constants n and K.

(B) Determination of Heat of Adsorption of Acetic Acid on Charcoal

According to Langmuir, the form of isotherm appropriate to adsorption from solution:

$$\theta = \frac{kc}{1+kc} \quad (1)$$

where θ is the fraction of the solid surface covered by adsorped molecules and k is a constant at constant temperature. Now θ = N/Nm where N is the number of moles of adsorbate per gram of solid charcoal at an equilibrium solute concentration c and Nm is the number of moles per gram required to form monolayer. Making this substitution.

$$\frac{N}{Nm} = \frac{kc}{1+kc} \quad (2)$$

On rearrangement

$$\frac{C}{N} = \frac{C}{Nm} + \frac{1}{KNm} \qquad (3)$$

A plot of C/N versus C will yield a straight line with slope 1/Nm and interaction 1/kNm (at C = 0).

The heat of adsorption, Q_a is given by:

$$Q_a = RT^2 (d \ln C/ dT)_\theta \qquad (4)$$

On integration:

$$Qs = \frac{RT_1T_2}{(T_2 - T_1)} \text{ x } \ln\left(\frac{C_2}{C_1}\right)_\theta \qquad (5)$$

If we know the temperature dependence of the equilibrium concentration C. For this purpose it is necessary to find the adsorption equilibrium for at least two temperatures (T_1 and T_2) for the same amount of θ.

Procedure:

1. Prepare the following stoke standard solutions:
   (A) 500 ml 0.5 N CH_3COOH
   (B) 1000 ml 0.1N NaOH
2. Into six small flasks prepare 100 ml of each of 0.2, 0.15, 0.12, 0.09, 0.06 and 0.03N CH_3COOH solutions by appropriate dilutions.

3. To each flask add one gram of charcoal, thermostat at 15 °C for 60 minutes with occasional shaking.
4. Filter each solution through a dry filter paper into a dry receiver rejecting the first few mis of filtrate.
5. Titrate 25 ml filtrate with NaOH solution.
6. Repeat steps 2-5 at 30 °C.

Plot C/N versus C, and evaluate K at 15 °C and 30 °C. From equation (1) calculate C_1 and C_2 at $\theta = 0.5$. Calculate the heat of adsorption of acetic acid on charcoal using equation (5).

Experiment:

Object:

To determine the surface adsorption of amyl alcohol from aqueous solutions using capillary rise method.

Apparatus: Capillary tube, thermostat of pyknometer

Theory:

Surface Excess: The concentration of a solute in a solution is different at the surface (solution-air interface) from that in the bulk. If a volume v of the solution at the surface constituting an area A, contains n` moles of the solute and the same volume of the solution in the bulk contains n moles of the same, the quantity, $\frac{n`-n}{A}$ is called the surface excess (Γ) of the solute. A positive surface excess is associated with the lowering of surface tension. The thermodynamic relationship between the surface tension and the surface excess is given by Gibb's familiar equation.

$$\Gamma = -\frac{1}{2.303RT} \cdot \frac{d\gamma}{d\log C}$$

where Γ is surface excess, i.e., number of moles of solute per cm^2 of surface in excess to the bulk concentration C; R the gas constant. Since the surface tension (dyne/cm) is a measure of the surface energy erg/cm^2, R should be expressed in ergs per gm molecule (8.37×10^7 erg). The negative sign signifies that

the surface tension decreases with increase of bulk concentration of solute. In order to determine Γ measurements of surface tension are made at different concentrations of solute. From the values obtained, the area per molecule at the surface at any solute concentration may be computed.

Procedure:

1. Prepare 100 ml 2% amyl alcohol in water (density of amyl alcohol 0.81 g/cm^3).
2. By appropriate dilution of the above solution prepare 1.0, 0.5, 0.25, 0.125 and 0.063% solutions. Thermostat the solutions at 20 °C.
3. Using the capillary rise method to determine the surface tension of the above solutions at 20°C.

Calculations:

1. For the determination of Γ two methods may be used.
   (a) Plot γ against log C including the point for pure water. Draw a smooth curve and determine the corresponding dγ/dlogC values for some chosen concentrations. Substitute them in Gibb's equation and calculate Γ.
   (b) Gibb's equation may be written in the form:

$$\Gamma = -\frac{C}{RT}\frac{d\gamma}{dC}$$

Plot γ against the bulk concentration C. A curve as shown in Fig. ( ) is obtained. The projection ab of the tangent to the curve at a point A on the y axis gives $C\frac{d\gamma}{dC}$ in dynes/cm. By substitution in the above equation Γ may be calculated.

2. Calculate the surface area per single solute molecule as $\frac{10^{16}}{\Gamma N}$ A^{02}; N is Avogadro's number.

PHASE EQUILIBRIA

COMPOSITION-TEMPERATURE DIAGRAMS

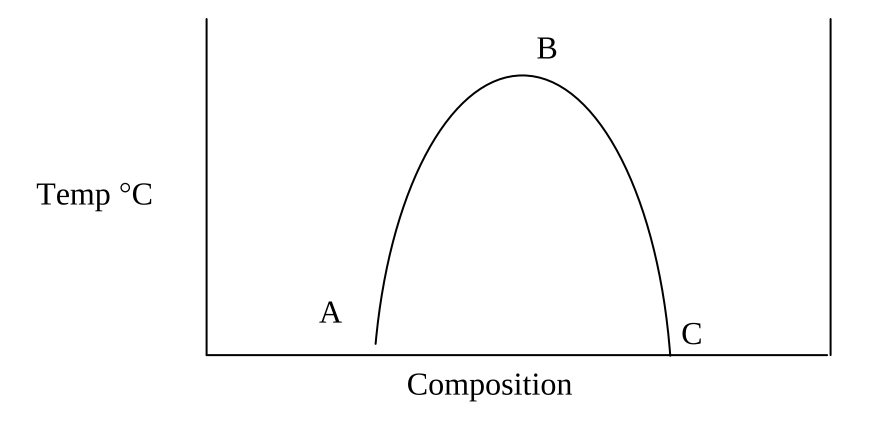
When two liquids are mixed together, one of the following cases may arise:

(a) The two liquids are completely miscible at all preparations yielding one homogenous liquid phase, for example alcohol and water.

(b) The two liquids are partially miscible yielding either one or two liquids phases, depending on the conditions, for example phenol and water.

(c) The two liquids are practically immiscible yielding always two distinet phases under ordinary conditions, for example carbon disulphide and water.

The mutual solubility of partially miscible liquids usually increases with temperature. In this case, the solubility curve exhibits a maximum at the critical solution temperature above which the two liquids become completely miscible at all proportions. For some liquid pairs such as ether and water, however, the mutal solubility decreases with temperature, and the solubility curve shows a minimum at the critical solution temperature below which the two liquids become completely miscible at all proportions. The temperature-composition diagram of the phenol-water system is shown in the following figure. Outside the area bound by the curve ABC there occurs one unsaturated homogenous liquid phase. Within that area, two liquid phases in equilibrium with each other coexist, one is water saturated with water.



Any point on the curve represents one saturated homogenous phase, the existence of the saturating phase should be assumed. As the solubility curve is hardly affected by pressure? The system may be treated as a condensed one of two components. For condensed systems the phase rule may be expressed as F=C-P+1; where F is the number of degrees of freedom, C the number of components and P and number of phases, outaide the area enclosed by the curve, since P = 1, therefore the umber of degrees of freedom F is a, which means that the temperature and concentration as variants, may be changed independently. For any point on the curve, P = 2, therefore F is 1, meaning that concentration must change with temperature. For the points enclosed within the curve, the situation is the same for any particular layer as for any point on the curve.

Experiment:

Determination of the critical solution temperature of the phenol-water system:

Procedure:

1- In a clean dry test tube weight accurately about 3 to 4g phenol.

2- Add the calculated volume of water so as to obtain a mixture of 70% phenol and 30% water by weight.

3- Cover the tube with a sork stopper carrying a thermometer and a stirrer, then place in a beaker containing water to serve as a bath.

4- Heat (or cool) gradually while the mixture is constantly stirred until the two layers disappear forming one homogenous layer. The two temperatures at which this occurs on passing from a lower to a higher temperature and the reverse, are recorded. These two temperature of the mixture used.

5- To the same mixture add the necessary volume of water so as to obtain a mixture of 60% phenol. Determine the miscibility temperature of the new mixture as described above.

6- Repeat, using mixtures containing 50, 40, 35, 25 and 15 phenol.

Calculations:

1- Record the volume of water used for each composition.

2- Plot miscibility temperature against percentage phenol for the various mixtures.

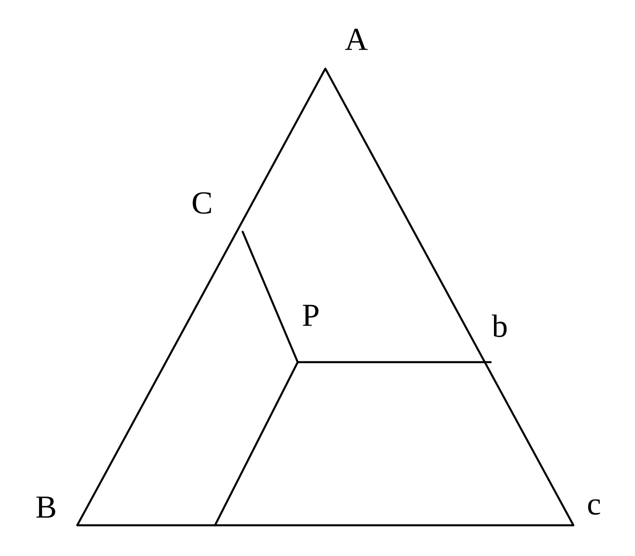
3- From the curve obtained find out the critical solution temperature and the corresponding compositions.

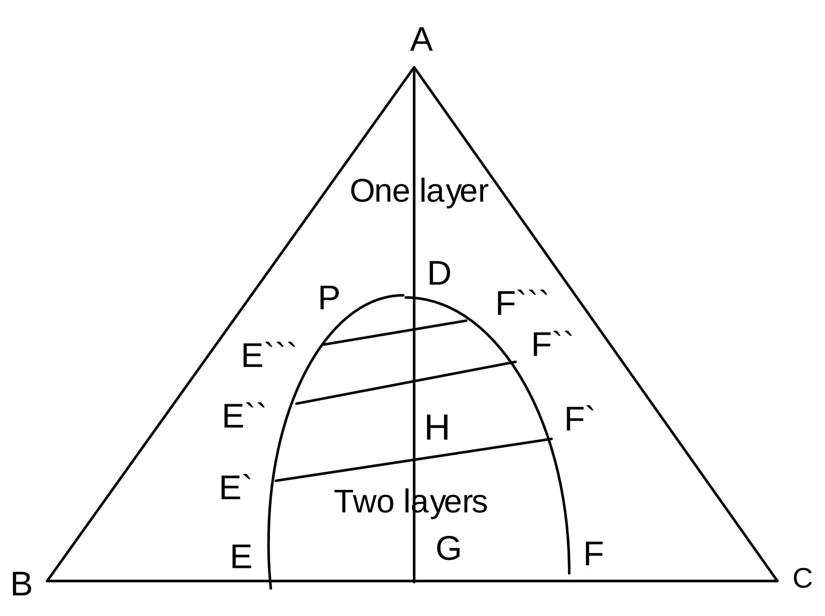
PHASE DIAGRAM OF A THREE COMPONENT SYSTEM CHLOROFORM-ACETIC ACID-WATER

Introduction:

With a system of three components, four variables are possible, this pressure, temperature, and two concentration terms (the ration of the third component will be automatically fixed). To simplify the study of phase properties. The system is treated as a condensed one at a constant temperature. In which case the pressure and temperature as variables, are dispensed with the phase value expression reduces hence to F = C-P under study conditions. The phase properties are best defined by using the triangular diagram. On an equilateral triangle (figure below). The apexes A, B and C represent pure components (100 x each). A point, P inside the triangle represents the composition of A, S and C of percentage respectively proportional to all lengths of the lines Pa, Pb, Pc drawn parallel to the sides of the triangle.

When systems comprise three liquids there may be samples miscibility through this is relatively rare. It is usually to find one, two or three pairs acid-chloroform-water, the water and chloroform are only partially miscible, and the equilibrium diagram, at constant pressure and temperature is illustrated in the following figure.





Ternary systems, one pair partially miscible

In the concentration ranges BE and CF the mixtures of B and C from true solutions between E and F the system will produce two liquid layers of varying amounts but of compositions E and F. Point G represents two layers in the ratio:

$$\frac{Weight\ of\ layer\ of\ composition\ E}{Weight\ of\ layer\ of\ composition\ f} = \frac{GF}{GE}$$

Acetic acid is miscible with both water and chloroform and as might be expected, its addition to the mixture cases more water to dissolve in the chloroform layer and more chloroform in the water layer. Thus, line GA shows the effect of adding acetic acid to the original two-layer system G. When the overall composition of the ternary system correspond to point, H the two conjugate solutions present have composition E` and F` in the ratio.

$$\frac{Weight\ of\ layer\ of\ composition\ E`}{Weight\ of\ layer\ of\ composition\ F`} = \frac{HF`}{HE`}$$

A series of experimental determinations would provide data for a series of much points, E`, F`, E``, F`` and so on, and the claired curve could be plotted. Thus is a bimodal curve, that is, it is constructed from data in pairs. Then any overall

composition represented by a point inside the curve would yield a two layer while all mixtures elsewhere in the triangle would form single-phase solutions. The relative amounts of the two layers vary as more acetic acid is added. The acid distributing itself between the layers, making them more alike, eventually one layer disappears and sufficient acid has then added to achieve complete miscibility. This occurs at point, P on the boundary curve for the original mixture A.

The composition points E`, F` and E``, F`` for the conjugate solution are joined by the lines these are rarely parallel to the sides of the triangle but rotate as in the figure. They shorten and finally varnish at P. The plait point of the system while the biondal curve may be determined by starting with varian mixtures of compositions between E and F. The data for P can only be found from one particular mixture K. The original G for example would only yield data along the curved suctions FD and EE``.

APPARATUS AND CHEMICALS

5 stopped bottles, a burettes, chloroform and acetic acid

Procedure:

1. Put in each of the 5 bottles a mixture of chloroform and acetic acid with following composite on:

Bottle	1	2	3	4	5
Chloroform	1.7	3.3	6.6	10.0	13.3
Acetic acid	21.4	19.0	14.3	9.5	4.8
Water					

2. Add distilled water from the buretis to the continuous of such bottle (drop by drop) while shaking vigorously until the turbidity appears. At this point record the volume of distilled water needed for each bottle and insert in the proper place in the above table.
3. Knowing the volume of each substituted in each bottle and its density:

$d_{HA} = 1.05\ g/cm^3$

$dCHCl_3 = 1.5\ g/cm^3$

$dH_2O = 0.997\ g/cm^3$

The weight percentage for each component, can be obtained as follows:

Wt.% of $CHCl_3$ in bottle (1)

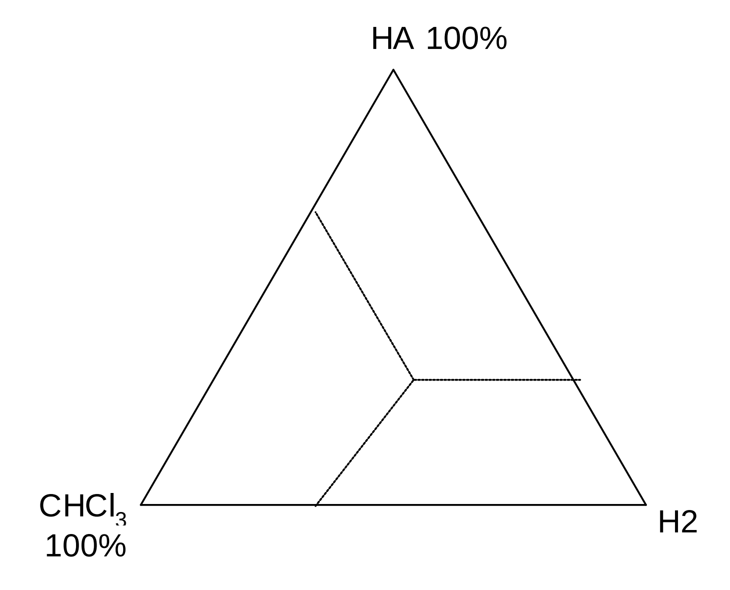
$$= \frac{1.7x1.5}{(1.7x1.5)+(21.1x1.05)+(V_{H2O}x0.997)}$$

where V_{H2O} is the volume of water needed to cause turbidity in bottle (1).

4. Tabulate your results as follows:

Bottle	1	2	3	4	5
Wt.% $CHCl_2$					
Wt. % HAC					
Wt.% H_2O					

5. Draw the phase diagram of the suitable as an equilibrium triangle as represented below.



THE NATURE OF COPPER-AMMONIA COMPLEX IN AQUEOUS SOLUTIONS

Investigation of the distribution coefficient of ammonia between aqueous copper sulphate solution and chloroform serves to indicate complex formation between copper sulphate and ammonia. The deviation of the distribution coefficient of ammonia from its normal value for pure water and chloroform measures the extent of complexity between copper sulphate and ammonia.

Experiment: Part (A)

Determination of the partition coefficient of ammonia between chloroform and water

Procedure:

1- Prepare 250 ml N ammonia, 250 ml of approximately 0.5N HCl and 100 ml of exactly 0.5N Na_2CO_3. Standardize HCl against Na_2CO_3, and the ammonia solution against HCl using methyl orange as indicator. By appropriate dilution prepare 250 ml of exactly 0.025 N HCl.

2- In a separating funnel shake up 50 ml ammonia solution with 25 ml chloroform, keep in a thermostat at 15 °C for at least 30 minutes with occasional shaking.

3- After complete separation, withdraw the bottom layer (chloroform) in a dry stopper flask. Determine the amount of ammonia in chloroform by pipetting up 10 ml into a conical flask containing 100 ml water, then titrating directly with 0.025N HCl. Determine the amount of ammonia in the aqueous layer by pipetting 10 ml into a conical flask, dilute with water and titrate with 0.5N HCl.

Calculations:

The distribution coefficient K is obtained from the expression.

$$K = \frac{Concentration\ of\ ammonia\ in\ chloroform}{Concentration\ of\ ammonia\ in\ water}$$

Concentration may be expressed in gram ammonia per liter.

Experiment: Part (B)

Determination of the nature of the copper-ammonia complex

Procedure:

1- Prepare 100 ml of exactly 0.1M copper sulphate solution.

2- In a separating funnel shake up 40 ml N ammonia solution with 10 ml of copper sulphate solution and 25 ml chloroform. Keep in a thermostat for at least 30 minutes with occasional shaking.

3- Separate off 10 ml of the chloroform layer and determine the amount of ammonia by titration with 0.025 N HCl as described in experiment part (A).

Calculations:

1- Knowing the distribution coefficient of ammonia between chloroform and pure water as obtained in experiment (A), and the concentration of ammonia in chloroform as determined in experiment (B), the concentration of free ammonia in the copper sulphate solution is calculated.

2- The difference between the total ammonia and free ammonia gives the amount of fixed ammonia.

3- Knowing the concentration of copper sulphate, n, the number of coordinated ammonia molecules at $Cu(NH_3)_n^{-2}$ is computed.

Distribution of Acetic Acid Between Benzene And Water
Strength of The Hydrogen Bond

The variation with concentration of the partition coefficient of acetic acid between benzene and water at different temperatures may be used to determine the strength of the hydrogen bridges responsible for double molecule formation in benzene according to:

$$2\,CH_3.COOH \rightleftharpoons H_3C\text{-}C\begin{matrix} {\diagup\!\!\!\!=}O\text{---}H\text{-}O{\diagdown} \\ {\diagdown}O\text{-}H\text{---}O{=\!\!\!\!\diagup} \end{matrix}C\text{-}CH_3$$

The lines represent the two hydrogen bridges which join the two molecules.

In strong aqueous solutions, acetic acid exists almost as single unionized molecules. In benzene, a considerable amount of dimerization occurs giving:

$$\frac{\text{Water HAc } (C_w)}{\text{Benzene HAc } (C_1) \rightleftharpoons 1/2\ (\text{HAc})_2(C_2)}$$

C_w and C_1 are the monomer concentrations in water and benzene respectively; C_2 that of dimmer in the benzene layer. The total concentration in benzene, expressed as monomer, is $C_B = C_1 + 2C_2$. Setting up the equilibrium equation for the system, it follows:

$$K_1 = \frac{C_1}{Cw} \quad , \qquad K_2 = \frac{(C_1)^2}{C_2}$$

where K_1 is the partition coefficient of acetic acid monomer between benzene and water, K_2 the equilibrium constant for acetic acid association in benzene. Hence,

$$C_B = C_1 + 2C_2$$

$$= K_1C_w + \frac{2C_1^{\ 2}}{K_2}$$

$$= K_1C_w + \frac{2K_1^{\ 2}C_w^2}{K_2}$$

$$\frac{C_B}{Cw} = K_1 + \frac{2(k_1)^2}{K_2} . C_w$$

The energy, ΔH, required to break the two bonds joining the two molecules in the dimmer, is obtained using the Van't Hoff iso

$$\Delta H = R \left(\frac{T_1 - T_2}{T_2 - T_1}\right) x\ 2.303, \log \frac{K_2 (at\, T_2)}{K_2 (at\ T_1)}$$

The strength of a hydrogen bridge is one half ΔH.

Experiment:

Determination of the strength of the hydrogen bridges responsible for the of acetic acid in benzene

Procedure:

1- Prepare 100 ml of reach of exactly 0.1 N $NaCO_3$. 0.1N. HCl, 0.1N NaOH and = NCH_2COOH. Standardize HCl against Na_2CO and NaOH against HCl. By appropriate dilution prepare 250 ml of each of exactly 0.05 N and 0.02N NaOH solutions.

2- In a dry stoppered tube, shake up 30 ml benzene with 25 ml normal acetic acid. in another tube shake up 30 ml benzene with 15 ml normal acetic acid and 10 ml distilled water. Keep in a thermostat at 10 °C for at least 30 minutes with occasional shaking and leave until the two layers separate.

3- The concentration of acetic acid in the benzene layer, Ca is determined by pipetting out 10 ml into a conical flask containing some distilled water and titrating with 0.02 N NaOH using phenolphthalein as indicator.

4- Pipetic out 10 ml of the aqueous layer and dilute to 100 ml in a measuring flask. Use 10 ml of this solution to determine the concentration of acetic acid in the aqueous layer, C_n by titrating with 0.05 N NaOH. Express concentrations in moles/litre.

5- Repeat step (2) at 20 °C and 30 °C, and determine C_n and C at each temperature as described in steps (3) and (4).

Calculations:

1- P lot C_B/C_w against Cw: the intercept of the line obtained is K_1, and the slope is $2(K_1)^2/K_2$.

2- Knowing the value of K_1, the value of K_2 is obtained.

3- Substitute in the Van't Hoff isochore to obtain ΔH.

Obtain A Value For The Equilibrium Constant And The Standard Free Energy Change For The Reaction

$I^- + I_2 \leftrightarrow I_3^-$

By The distribution method

Theory:

When a solute (iodine) is distributed between two immiscible liquids, at equilibrium, the ratio of the concentrations of the same molecule species of the solute in the two liquids is a constant for that system. Thus, for iodine distributed between CCl_4 and water, D is given by:

$$D = [I_2] / [I_2]_w$$

(1)

Where the subscripts and we refer to solvent and water respectively.

Iodine dissolved in iodide solutions exists largely as the iodide ion I_3. There exists an equilibrium between the iodine, iodide and thetriiodide in a solution such that $I^- + I_2 \leftrightarrow I_3^-$. The value of the equilibrium constant K, for this reaction is given by:

$$K = [I_3^-]/[I^-][I_2]$$

(2)

You are going to determine the equilibrium constant of this reaction by shaking a solution of known K_1 concentration

with a solution of iodine in CCl_4. In the aqueous solution, the todide, and the total iodine are known. The total to line, $[I_2]$ could be determined by titration against a standard $Na_2S_2O_3$ solution. The total iodine is of course equal to $[I_2]$ + $[I_3]$. The concentration of free iodine in the aqueous layer $[I_2]_w$, could be calculated using the value of the distribution coefficient D.

Materials:

(A) 0.1M solution of KI (250 ml).

(B) 0.05M solution of I_2 in CCl_4.

(C) 0.01N $Na_2S_2O_3$ (250 ml).

Procedure:

1. In a clean dry test tube introduce 40 ml of distilled water and 20 ml of 0.05M solution of iodine in CCl_4. In a second tube place 40 ml of 0.1M KI solution and 20 ml of 0.05M solution of iodine in CCl_4. Stopper the two tubes, shake vigorous and place them in a thermostat at 25 °C. Allow them to stay for at least one hour in thermostat with occasional shaking.
2. After the two liquids in each tube has separated into clear homogerous layers, pipette out a 10 ml sample from the aqueous layer into a conical flask containing about 10 ml of 0.1M KI. Pipette 5 ml sample of the

CCl_4 layer into a second control flask containing about 5 ml of the KI solution.

3. Titrate each of these samples with thiosulphate solution using starch is indicator. In the titration of the CCl_4 layer, shake the flask vigorously after adding the thiosulphate solution.

Calculations:

1. Compute the molar concentration of iodine in the aqueous and the solvent layers.
2. Calculate the distribution coefficient D in the first tube.
3. the titration of the aqueous layer in the second tube gives $\sum[I_2]$ the total titrstable iodine.

   The titration of the solvent layer in the second tube gives $[I_2]$, and the total potassium iodide [KI] is known:

$$\sum[I_2] = [I_2]_w + [I_3^-] \qquad (3)$$

$$[KI] = [I^-] + [I_3^-]$$

(4)

therefore, $$[I_2]_w = [I_2]/D \qquad (5)$$

knowing the value of D, calculate $[I_2]_w$ from equation (5). From equation (3) and knowing $\sum[I_2]$ and $[I_2]_w$ calculate $[I_3^-]$. Using this value and KI calculate $[I^-]$. Hence, calculate the equilibrium constant from equation (2)

4. Determine the standard free energy change from the equation:

$$\Delta G^\circ = - RT \ln k$$

where R is the gas constant amounting to 1.98 cal. mol^{-1} deg^{-1}, and T is the absolute temperature.

Partial Molal Properties Of Solutions

The accurate determination of the density of a liquid and the precise mathematical treatment of the properties of solutions are studied.

Theory:

The quantitative study of solutions has been greatly advanced by the introduction of the concept of partial molal quantities. A property of a solution, e.g., the volume of a mixture of alcohol and water, changes continuosly as the composition is changed, and considerable confusion existed formerly in exposing these properties as a function of composition. A partial molal property of a component of a solution is defined as follows. Let Y represent any extensive properly of a binary solution, at constant temperature and pressure, Y when will be a function of the two independent variables n_1 and n_2, which represent the numbers of moles of the two components present. The partial molal property of component is then defined by the relation.

$$\overline{Y}_1 = \left(\frac{\partial Y}{\partial n_1}\right)_{n2,T,P} \quad (1a)$$

Similarly for component 2,

$$\overline{Y}_2 = \left(\frac{\partial Y}{\partial n_2}\right)_{n1,T,P}$$

(1b)

The partial molal quantity may be designed by a par above the letter representing the property, and by a subscript, which indicates the component in which the value refers. The usefulness of the concept of partial molal quantities lies in the fact that it may be shown mathematically[1,2,4] that:

$$Y(n_1, n_2) = n_1\overline{Y}_1 + n_2\overline{Y}_2 \qquad \text{T, P constant} \qquad (2)$$

Any extensive property of the solution may be expressed in this manner in terms of partial molal properties, which themselves are functions of the concentration of the solution, the temperature, and the pressure and must be evaluated by means of experimental measurements. The activity of α_1 of a component of a solution is defined in terms of its relative partial molal free energy C_1-C_1^o and the calculation of heats of reaction for solution systems requires a knowledge of the relative partial molal enthalpies H_1-H_1^o for all the components. The superscript refers to the standard state.

In the case of the volume of the solution, Eq. (2) gives directly

$V = n_1\overline{V_1} + n_2\overline{V_2}$ T, P constant

The partial molal volumes V_1 and V_2 may be evaluated from density measurements on the solutions. The graphical method is described fully by Lewis and Randall may be used in the treatment of the data, of these e, the use of the apparent molal volume ϕ_Y is particularly convenient for binary Y solutions.

The apparent molal volume is defined by the relation:

$$\phi_Y = \frac{V - n_1\overline{V_1^o}}{n_2} \quad \text{T, P constant}$$

(3)

volume of solution containing n_1 moles of component 1 and n_2 moles of component.

V_i = molar of component 1 at given T, P since $V = n_2\,\phi_V + n_1V_1^o$.

$$V_1 = \left(\frac{\partial V}{\partial n_1}\right)_{n2,T,P} = \phi_Y + n_2\left(\frac{\partial \phi_V}{\partial n_2}\right)_{n1,T,P}$$

(4a)

and

$$V_1 = \frac{V - n_2V_2}{n_1} = \frac{1}{n_1}\left[n_1V_1^0 - n_2^2\left(\frac{\partial\phi_V}{\partial n_2}\right)n_1, T, P\right] = \phi_Y + n_2\left(\frac{\partial\phi_V}{\partial n_2}\right)_{n1,T,P} \quad (4b)$$

In terms of the experimentally measured density ρ and the molecular weights M_1 and M_2 of the two components.

$$\phi_V = \frac{1}{n_2}\left(\frac{n_1M_1 + n_2M_2}{\rho} - n_1V_1^o\right) \quad (5)$$

when the molal concentration scale is used, n_2 = m, the molality, and n_1 is equal to the number of moles of component 1 in 1000 g of solvent, so that:

$$\phi_V = \frac{1}{m}\left(\frac{1000 + mM_2}{\rho} - \frac{1000}{\rho_1}\right) = \frac{1000}{nt\rho\rho_1}(pt - p) + \frac{M_2}{\rho} \quad (6)$$

where ρ_1 = density of pure component 1

ρ = density of solution of molality m of component 2 having molecular weight M_2.

The second expression is particularly convenient for actual calculations.

The use of the apparent molal volume in this determination is advantageous because the error involved in the graphical determination of the derivative of a function is encountered only in the evaluation of the tem giving the difference between the partial molal volume and the apparent molal volume.

The partial molal volume may be visualized by considering a large reservoir of a solution of given composition, so large that the addition of one more mole of a component will not appreciably alter the concentration. If now 1 mole of component 1 is added to this large reservoir of solution, the increase in the volume of the solution is equal to the partial molal volume of component 1 at the indicated concentration, temperature and pressure. The magnitude of the partial molal volume depends upon the nature of the interactions between the components of the solution under the given conditions, the effects of these interactions are difficult to predict theoretically, but the overall result is readily expressed mathematically, as already shown. In the special case of an ideal solution, the partial molal volume of any component at the temperature and pressure of the solution.

The concept of the partial molal quantity may, of course, be applied to solutions containing more than two

components. The extension of Eqs. (1) and (2) to the general case is discussed in detail elsewhere.

Apparatus, pycometers, thermostat: rapid analytical balance, six small glass stoppered bottles or flasks, sodium chloride.

Procedures:

Solutions of sodium chloride in water containing approximately 2, 4 8, 12 and 16 percent sodium chloride by weight are prepared. The salt and water are weighed out accurately into a weighing bottle or glass stoppered flask, care being taken to prevent evaporation of the volatile solvent. A total volume of about 75 ml of each solution is required for the excution of duplicate determinations.

The density of each solution is determined accurately at 25 °C. A pycnometer of the Weld or Ostwald-Sprengel type shown in Figure below may be used. The pycynometer is dried carefully, weighed, then filled with distilled water, and placed in the thermostat for 10 to 15 min.

The Weld pycnometer is initially filled to bring the liquid level about halfway up the throat T of the reservoir R. the pycnometer is placed in the thermostat with the cap C in position to prevent on the tip of the plug is wiped off with a piece of filter paper, care being taken to avoid removing liquid

from the plug capillary in the process. The pycnometer is then removed from the thermostat, wiped dry with a lintless cloth, and the (dried) cap C put in place. It is allowed to stand in the balance case for a few minutes before being weighed.

With the Ostwald-Sprengel pycnometer, the quantity of liquid is adjusted so that the liquid meniscus is at the mark on the horizontal capillary when the other capillary arm is filled. This adjustment may be made by tilting the completely filled until slightly and withdrawing liquid slowly from the other capillary by touching a piece of filter paper to it. The pycnometer is removed from the thermostat and wiped dry with a lintless, cloth, and the caps placed on the capillary arms. It is allowed to stand in the balance case for a few minutes before being weighed.

For the best results, it is suggested that the temperature of the balance room be not much above that of the thermostat. Also, there is often difficulty with "creeping" of the salt solution during storage. It is preferable to make up the solutions and measure the densities on the same day.

In this fashion, duplicate determinations are made of the weight of liquid required to fill the pycnometer at the at thermostat temperature, for water and for each of the solutions

previously prepared. Two pycnometers may be used advantage, so that one may be weighed while the other is in the thermostat.

Calculations:

The weights of the water and of the various salt solutions held by the pycnometers are corrected to vacuum as described. The density of water at 25 °C is taken as 0.99707g ml^{-1} for the calculation of the volumes of the pycnometers. The density of each solution is then calculated by dividing its vacuum weight by the appropriate pycnometer volume.

The concentration of each solution is expressed in terms of the molal concentration scale, and the apparent molal volume is determined at each concentration. The uncertainty in the apparent molal volume introduced by an uncertainty of 0.02 percent in the density is computed for each solution.

By means of Eqs. (4a) and (4b) the partial molal volumes of solute and solvent are evaluated at each concentration. In this case n_2= m, the molality, and n_2, the number of moles of solvent associated with n_2 moles of solute, is equal to 55.51, that is 1000/18.016. It is convenient in the

case of an electrolytic solution to plot ϕ_V against m^1 instead of against m and to utilize the relationship.

$$\left(\frac{\partial \phi_V}{\partial m}\right)_{n1,T,P} = \frac{4}{2m^1}\left[\frac{\partial \phi_V}{\partial (m^1)}\right]_{n1,T,P}$$

(7)

A second method is also used for the evaluation of V_2. The volume of solution containing 1000g of solvent, is plotted against the molality m.



Chapter 4

Electrochemistry

Inhibition of Corrosion of Zinc in Sulfuric Acid Solutions Using Weight Loss Technique

The evaluation of the corrosion rate of metals is very important to overcome the corrosion problem. In this experiment a trial is made to inhibit the corrosion of Zn metal using potassium permanganate and potassium dichromate.

Procedures:

1- Polish the zinc specimen with emery papers of different grades to a mirror surfaces, degrease with acetone, wash with running distilled water and leave it to dry in a dissicator.

2- Prepare a series of 0.5M sulfuric acid solutions with different additive concentrations.

3- Weight accurately the specimen and hang it in the corrosive solution. Use three specimens in the same solution.

4- After an appropriate time take the specimen out of the solution, wash it with running distilled water, dry it between two filter papers and weight it secondary. Return the specimen to the solution and repeat this step for different time periods.

5- Compute the weight loss of the specimens and calculate the main weight loss for the corresponding time.

6- Draw a relation between weight loss in grams and the elapsed time. the slope of the curve will be the rate of corrosion in gm/hr.

7- Calculate the corrosion rate in millimeter per year (mpy) using the following equation:

$$\text{mpy} = \frac{(543 x wt.loss)}{d.A.t}$$

where d is the density of metal, A is the surface area of it.

Measurement of Corrosion Rate of Zinc in Sulfuric Acid Solutions Using Weight Loss Technique

The evaluation of the corrosion rate of metals is very important to overcome the corrosion problem. In this experiment the corrosion rate of Zn metal is calculated using weight loss technique.

Procedures:

1- Polish the zinc specimen with emery papers of different grades to a mirror surfaces, degrees with acetone, wash with running distilled water and leave it to dry in a dissicates.

2- Prepare a series of sulfuric acid solution with different concentrations.

3- Weight accurately the specimen and hang it in the corrosive solution. Use three specimens in the same solution.

4- After an appropriate time take the specimen out of the solution, wash it with running distilled water, dry it between two filter papers and weight it accurately. Return the specimen to the solution and repeat this step for different time periods.

5- Compute the weight loss of the specimens and calculate the main weight loss for the corresponding time.

6- Draw a relation between weight loss in grams and the elapsed time. The slope of the curve will be the rate of corrosion in gm/hr.

7- Calculate the corrosion rate in millimeter per year (mpy) using the following equation:

$$\text{mpy} = \frac{(543 x wt.loss)}{d.A.t}$$

where d is the density of metal, A is the surface area of it and t is the time comment on your results.

Measurements of Corrosion Rate of Zinc in Sulfuric Acid Solutions Using Thermometry Technique

The evaluation of the corrosion rate of metals is very important to overcome the corrosion problem. In this experiment the corrosion rate of Zn metal is calculated using thermometry technique.

Procedure:

1. Polish the zinc specimen with emery papers of different grades to a mirror surfaces, degrease with acetone, wash with running distilled water and leave it to dry in a dissicator.
2. Prepare a series of sulfuric acid solution with different concentrations.
3. Immerse the specimen in the sulfuric acid solution in a mylius tube, and record the temperature (T_1) instantaneously.
4. Record the temperature at different time periods.
5. Draw the relation between the temperature and time.
6. From the figure calculate the maximum temperature (T_{max}) and the time corresponding to it (t).
7. Calculate the rate of corrosion (R) from the following equation:

$$R = \frac{(T_{max} - T_1)}{t}$$

Comment on your results

Inhibition of Corrosion Rate of Zinc in Sulfuric Acid Solutions Using Thermometry Technique

The evaluation of the corrosion rate of metals is very important to overcome the corrosion problem. In this experiment the inhibition of corrosion rate of Zn metal by potassium permanganate and potassium dichromate is calculated using thermometry technique.

Procedure:

1. Polish the zinc specimen with emery papers of different grades to a mirror surfaces, degrease with acetone, wash with running distilled water and leave it to dry in a dissicator.
2. Prepare a series of sulfuric acid solutions with different additive concentrations.
3. Immerse the specimen in the sulfuric acid solution in a Mylius tube and record the temperature (T_1) instantaneously.
4. Record the temperature at different time periods.
5. Draw the relation between the temperature and time.
6. From the figure calculate the maximum temperature (T_{max}) and the time corresponding to it (t).
7. Calculate the rate of corrosion (R) from the following equation:

$$R = \frac{(T_{max} - T_1)}{t}$$

Calculate the inhibition efficiency (I.E.) for each compound using the following equation:

$$(I.E) = \frac{(R_f - R_1)}{R_f}$$

where R_f and R_i are the rate of corrosion in uninhibited and inhibited solutions, respectively.

Comment on your results.

Experiment:

Object:

To determine the ionization constant of acetic acid.

Apparatus:

Conductance bridge, beaker, pipette and measuring flask and IN acetic acid.

Theory:

The apparent equilibrium constant of acetic acid (CH_3COOH) is given by:

$$K`_a = \frac{[H_3O^+][OAc`]}{[HOAc]} = \frac{\alpha^2 C}{1-\alpha}$$

(1)

The degree of ionization α, at any molar concentration C, can be calculated approximately from the measured equivalent conductance at that concentration (Λ) and the equivalent conductance at infinite dilution (A_o) using the following equation:

$$\alpha = \frac{\Lambda}{\Lambda_o}$$

(2)

The value of Ao of acetic acid can not be obtained by extrapolation but calculated form the ionic conductance of H^+ and OAc` ions.

A_o (HOAc) = $\lambda H^+ + \lambda OAc^-$ = (349.8 + 40.9) = 390.7 ohm^{-1} cm^2 (3)

Substitution of Eq.(2) in Eq.(1) gives only an approximate value for $K`_a$ because Eq.(2) neglects the variation of ionic mobilities with ionic concentration. Eq.(2) can be modified to Eq.(4) to get a more accurate value for α,

$$\alpha = \frac{\Lambda}{\Lambda`}$$

(4)

where $\Lambda`$ is equivalent conductance of acetic acid due to the ions of completely ionized acid at the ionic concentration $\alpha$ C. The value of $\Lambda`$ can be calculated form

$$\Lambda` = \Lambda_o - (A + B\Lambda^o)\sqrt{\alpha C}$$

(5)

A and B are constant and equal to 60.2 and 0.229 respectively for water as solvent at 298.15 K. Substitution of Eq. (4) in Eq. (1) gives an accurate value of K_a.

Procedure:

1. Prepare and standardize 0.1N stock solution of acetic acid in conductivity water in the usual way.
2. Prepare a set of acetic acid solution (50 cm^3) each of concentration 0.1, 0.02, 0.005, 0.002, 0.001, 0.0005 and 0.0002N by dilution of original stock solution.
3. Measure the cell constant of conductivity cell.
4. Measure the specific conductivity of each solution of acetic acid after equilibrium at 25 °C in a thermostat for half an hour.

Calculations:

Cell constant = 0.99 cm^{-1}

Calculate the ionization constant, as follows:

i) Calculate specific conductivity K of each solution using the following Eq.

(Specific conductivity = cell constant x observed conductivity)

ii) Using the value of K, calculate equivalent conductance A for each solution using the following Eq.

$$A = \frac{1000k}{C}$$

iii) Calculate Λ\` for each solution using Eq.(5). Substituting α by Λ/Λ_o for each concentration. (Λ_o may be taken to be equal to 390.7 ohn^{-1} cm^2).

iv) Calculate α for each value of C using Eq.(4).

v) Substitute α in Eq. (1) to get K_a for each value of C.

vi) Tabulate the results and comment.

Results may be tabulated in the following manner

Serial No.	Conc. Of acetic, C mole dm^{-1}	Observed conductance ohm^{-1}	Equivalent conductance $ohm^{-1}\ cm^2$	$\alpha = \frac{\Lambda`}{\Lambda}$	$K`_a$ mole dm^{-3}	$K`_a$ (mean)
1						
2						
3						
4						
5						
6						
7						
8						
9						

Electrochemistry

Decomposition Voltage

The decomposition voltage of a solution may be defined as the minimum applied voltage necessary to cause continuous electrolysis of the solution. For the dilute aqueous solutions of acid and such as HNO_3, H_2SO_4, NaOH, and the decomposition voltage at inert potassium electrodes, is almost the same and amounts approximately to 1.7 volt. This is reactly explained by the fact that in all these the two main electrochemical specimens of mechanism, are the hydrogen at cathode and oxygen at anode. Theoretically, this voltage would be only infinitsmally greater than that of the reversible oxygen-hydrogen cell; 1.23 volt. The difference, however, is contained by the extent of over-voltage needed for the irreversible electrode reactions to proceed at a certain rate.

Before free electrolysis commences, a small current, the residual current, is usually observed. This serves to build-up the double layer at the electrode-solution interface as a requisite for free electrolysis. Extraneous factors such as deposition of impurities or cathodic reduction of dissolved oxygen, may cause some interference. However, in absence of such factors, the residual current is in fact very small.

The electrical circuit commonly employed for the determination of decomposition voltage is as shown in Figure.

Experiment:

Determination of the decomposition voltage of a normal sulfuric acid solution between two platinum electrodes

Procedure:

1. Prepare 50 ml of approximately 1N H_2SO_4. Place in a beaker, and insert two platinum sheet electrodes 0.5 cm^2 area each. The solution is constantly stirred with a current of purified hydrogen gas to avoid interference by dissolved oxygen.
2. Connect the electrodes to a 4-volt battery as an external source through a potential divider (sliding resistance R inserting a voltammeter (V) and a milliameter (A).
3. The sliding contact of (R) is first placed near end (a) so that a small e.m.f. is applied. Record current and voltage.
4. Move the contact a steps towards end (b) and record current and voltage at each step. Continue until evolution of gases at the electrode is visible.

Calculations:

1. Construct a current-voltage curve by plotting the observed currents against the applied voltage.
2. Extrapolation of the steep part of the curve to zero current defines the decomposition voltage.

Calculation of Electrochemical Cell Potential

Objective:

Upon completion of this laboratory experiment, the student technician will be able to calculate electrochemical cell potentials.

Material:

5. Copper, zinc, lead, aluminium electrodes
6. ..
7. solution (0.1 M)
8. Zinc nitrate solution (0.1 M)
9. Lead nitrate solution (0.1 M)
10. Measured potassium nitrate solution
11. sodium sulfide solution (0.1 M)

Theory:

An oxidation reduction reaction (redox reaction) such as:

$$Zn_{(s)} + Cu^{+2}{}_{(aq)} \rightarrow Zn^{+2}{}_{(aq)} + Cu_{(s)}$$

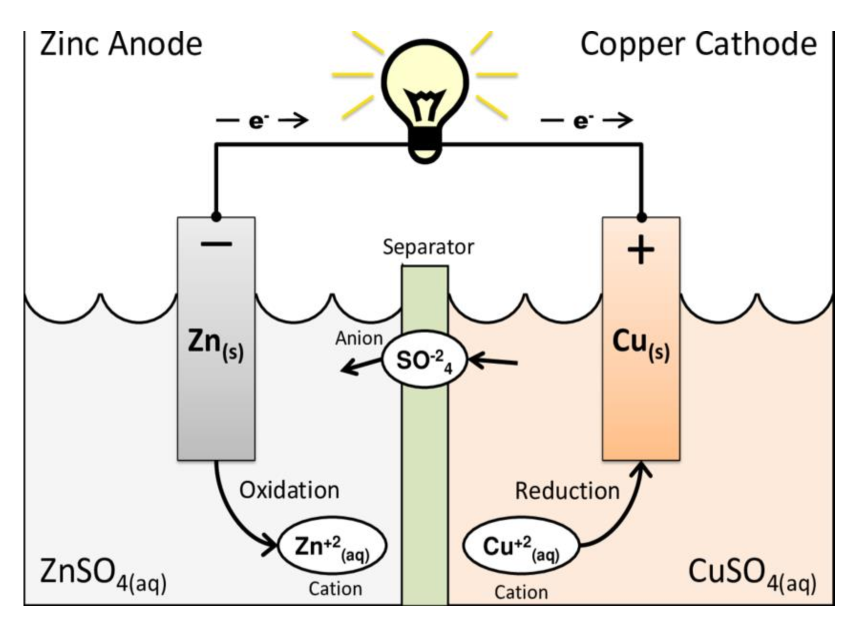
Can be separated into two half-reactions, called half-cell reactions.

$$Cu^{+2}{}_{(aq)} + 2e \rightarrow Cu_{(s)}$$

$$Zn_{(s)} \rightarrow Zn^{+2}{}_{(aq)} + 2e$$

The first half-cell reaction is the reduction half-cell, or the gain of electrons. The second half-cell reaction is the oxidation half-cell, or the loss of electrons.

This reaction can be carried out as shown in the following figure such that components of the oxidation and reduction half-cells are not mixed together, and that the potential of the reaction can be measured. In such a case, the reaction takes place very slowly since the voltameter has a very high resistance to electric current.



Such a cell can be represented by:

$Zn_{(s)}$ Zn^{+2} (1.0M) Cu^{+2} (1.0M) $Cu_{(s)}$

The measured potential for this cell, when the concentration of Cu^{+2} and Zn^{+2} are 1.0M each (or have the same concentration) is 1.10V. This value is referred to as standard voltage which indicates the voltage observed when all species are in their standard states (1.0M for species in solution, and 1.0 atm pressure for gases). Most commonly, values are measured at 298 K (25 °C).

The cell potential E``, can be calculated from the two half-cell potentials:

Zn + 2e, E^o + 0.76 V oxidation potential

(1M) + 2e → $Cu_{(s)}$, E^o = 0.34 V Reduction potential

$Zn_{(s)} + Cu^{+2}$ (1M) → Zn^{+2} (1M) + Cu(s) $E_o = 0.76 + 0.34$

$E_o = 1.10$ V

Cell potentials can be calculated from cell potentials and from the convention $E^o = 0$ for the half-cell:

Half (1M) + 2e → H_2(g) (atm), at all temperatures.

Electrode potentials are defined so that they do not depend on the number of molecules, ions, or electrons. It is intensive property. The electrode potentials are tabulated for the reduction half-cell reactions and are commonly at 298 °K.

When a cell reaction is written so that E`` is positive, the reaction will proceed spontaneously from left to right when all components are in their standard states.

Procedure:

1- Make a complete cell of the type shown in the figure, place 20 ml of 0.1M $Zn(NO_3)_2$ solution and 30 ml of 0.1 M $Cu(NO_3)_2$ solution in separate 100 ml (or 150 ml) beakers obtain a zinc and copper plate from the store room, clean both sides of each plate (electrode) with a strip of sand paper.

2- Fill a U-tube with saturated KNO_3 solution and insert loose cotton plugs soaked with the saturated KNO_3 solution in the ends of the tube leaving no air bubbles, the U-tube across the beakers as a salt-bridge.

3- Insert the metal plates in the solutions of their own ions.

4- Attach the appropriate electrodes to the voltameter terminals, using connecting wires, and read the voltage.

5- Remove the wires connecting the cell to the voltammeter and short circuit the cell with a single piece of wire. What chemical reaction is taking place?

   Which way are the electrons flowing?

   What changes do you observe that confirm a chemical reaction is taking place?

Now, while the single piece of wire is connected, attach the electrode to the voltameter terminals and read the potential.

Explain the large drop. (Note that the voltage reading is very small).

6- Repeat steps 1-4 making the following cells: Pb/Cu, and Pb/Zn. Record your readings in Table below.

When you have finished any part of this experiment, return the electrode to the store room, keep the salt bridge upside-down filled with saturated KNO_3 solution.

Calculations:

Table ( ): Cell potential

Cell	Measured	Calculated $E_{cell} = E^o_{cell}$-0.0591/n log Q
Zn/Cu		
Pb/Cu		
Pb/Zn		

For each cell you made, calculate its electrode potential using your textbook tablets. Compare the calculated values with those observed. Explain difference, if any.

Checklist:

1. …… your equipment and work benches before you leave.
2. …….all equipment to their proper storage area.
3. ……your answers to the questions, together with your data, calculations, and result before the next laboratory session.



Chapter 5

Thermochemistry

Thermochemical reactions:

Chemical reactions that are accompanied with heat absorption (endothermic reaction) or heat evolution (exothermic reaction)

Calorie: (Cal)*

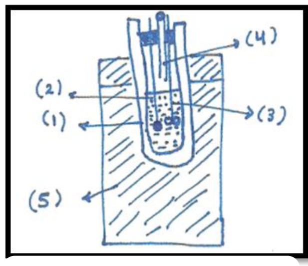
The amount of heat required to raise the temperature of 1g of water by 1 degree.

1 Cal =4.18 Joule

Calorimeter:*

An isolated system used to measure the heat evolved or absorbed from or by various thermochemical reactions.

(1) Dewar flask
(2) Thermometer (Beckmann, 0.1 °c)
(3) Stirrer (to mix the reactants)
(4) narrow tube plugged by glass wool (to introduce solutions into the flask)
(5) Isolating material



Calorimeter

Experiment (1):Determination of the heat capacity of the calorimeter or the calorimeter constant

The amount of heat (Q) in Joules:

$$Q = c' \, m \, \Delta t$$

Where
c′ = the specific heat capacity (J/g.deg.)
m = mass (g)
$\Delta t = (t_{final} - t_{initial})$ temperature different (deg.)

The specific heat capacity (C′): (J/g.deg.)

The amount of heat needed to raise the temperature of 1gram of a substance by 1deg.

The heat capacity (C): (J /deg.)

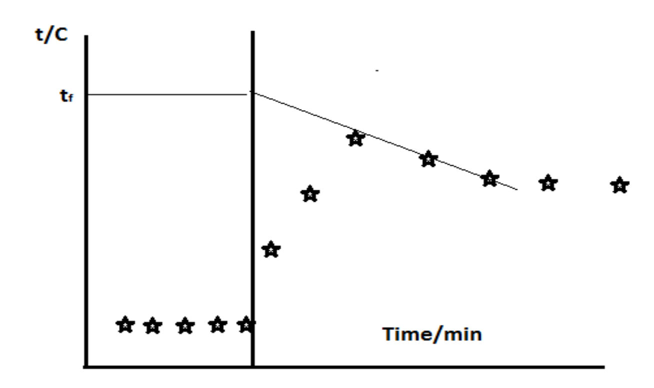
The amount of heat needed to raise the temperature of a substance by 1 deg.

$$\text{Heat capacity (c)} = \frac{Q}{\Delta T} = C' \times m$$

Procedure

1-Boil ~25 ml distilled water ($t_{initial} = t_1$=100°C)
2-In a dry and clean calorimeter, add 25ml of cold distilled water (V_2 =25ml) and record temperature every 1min. for 5min. ($t_{initial} = t_2$ =?)
3-Pour quickly the boiling water in to the calorimeter and record temperature every ½min. for 10 min.

4- Plot temp/°C vs. time /min and determine t_{final}, as shown
5-Measue the total volume of water in the calorimeter and determine V_1(volume of hot water) = V_{total} - V_2



Calculation

$Q_{\text{Lost by hot water}} = Q_{\text{gained by cold water}} + Q_{\text{gained by calorimeter}}$

Since:
$Q = c' \, m \, \Delta t$
$(c')_{H_2O}$= 4.18 J/g. deg.
$(density)_{H_2O}$ =1 g/mL thus, mass = volume, for only water

$$\Rightarrow (c' \, m \, \Delta t)_{\text{hot } H_2O} = (c' \, m \, \Delta t)_{\text{cold } H_2O} + (c' \, m \, \Delta t)_{\text{calorimeter}}$$

$$(4.18)(V_1)(100 - t_f) = [(4.18)(25)(t_f - t_2) + (\underline{c'm})\,(t_f - t_2)]$$

(Calorimeter constants)

Calorimeter constant or the heat capacity of the calorimeter:

$$(c'm) = c = \frac{v_1(100 - t_f)}{(t_f - t_2)} - 25$$

Experiment (2) Determination of the heat of neutralization of strong acid (HCl) by strong base (NaOH)

Heat of neutralization: $(\Delta H)_{neutralization}$ (J / mol)*

The amount of heat evolved when 1 equivalent of an acid (strong such as: HCl) is completely neutralized by 1 equivalent of a base (strong such as : NaOH)

It is equal to - 13.7 Cal / mol or -56.4 KJ/mol.

(the -ve sign indicates that heat is evolved i.e. exothermic reaction)

$H_3O^+ + HO^- \longrightarrow 2H_2O$ ΔH = -13.7 Cal/mol. Or - 56.4 kJ/mol.

*In case of the presence of a weak component (weak acid, acetic acid or weak base , NH_4oH) ΔH ≠13.7 Cal/mol. As part of the heat is consumed or emitted due to the complete ionization of the weak component (as will be seen in experiment (3))

procedure:

Part (A): Determination of the heat of dilution of HCl:

1-In a clean and dry calorimeter, add 25 ml of 1N HCL and record ($t_{initial}$)

2-Add 25ml of distilled H_2O, stir well and record (t_{final})

$$\Rightarrow \quad \Delta t = t_{final} - t_{initial}$$

3-Calculate the heat of dilution.

The heat evolved due to the acid dilution is gained by the aqueous acidic solution &the calorimeter:

$$Q_{dilution} = Q_{aq.HCl\ solution} + Q_{Calorimeter}$$

$$Q_{dilution} = (c'.m.\Delta t)_{aq.HCl\ solution} + (\underline{c'.m.}\ \Delta t)_{Calorimetr}$$

determined from exp.(1) ≈ 30 (J/deg.) ↓



$$Q_{dilution} = (4.18)(50)\ \Delta t + (30)\ \Delta t$$

Thus, $Q_{dilution}$ can be calculated. (≈ $Q_{dilution}$ =0)

Part (B): determination of the heat of neutralization of HCL with NaOH:
1-In a dry and clean calorimeter, add 25ml of 1N HCL and record the initial temperature (t_i) every 1 min. for 5min.
2- Add 25ml of 1N NaOH, stir well and record temperature every ½ min. for 10min .
3- Plot temp/°C vs. time/min, to get (t_f).

Total heat evolved $Q_{total} = Q_{dilution} + Q_{neutralization}$
$Q_{dilution}$ ⇨ determind from part (A)
$\therefore Q_{neutralization} = Q_{total} - Q_{dilution}$
But $Q_{total} = Q_{aqueous\ solution} + Q_{calorimeter}$
$Q_{total} = (c' \, m \, \Delta t)_{aq\ .soln} + (c' m \, \Delta t)_{Calorimeter}$

$Q_{total} = [(4.18)(50)(t_f - t_i)]+[(30)(t_f - t_i)]$

Finally, $\Delta H_{neutralization} = (Q_{neutralization} / n)$
n= no. of moles for acid or base = m v_L = $(1)(25x10^{-3})$ = 0.025 mol.

<u>Experiment (3) Determination of the heat of neutralization of weak acid (CH_3 COOH) by a strong base (NaOH) & heat of ionization of CH_3 COOH</u>

*The heat of neutralization of weak acids by strong bases is less than 13.7 Cal/mol because the weak acid becomes completely ionized before the neutralization reaction by absorption of heat.

$Na^+ + HO^- + (I-\alpha) CH_3C OOH + \alpha CH3COO^- + H^+ \leftrightarrows Na^+ + CH_3COO^- + H_2O$,

$\Delta H_{neutralization}$ <13.7 Cal/mol .

Where, α :fraction of ionized acid

Thus, $(1-\alpha)$:fraction of unionized acid

<u>procedure:</u>

1-determine $\Delta H_{neutralization}$ of acetic acid by NaOH as exp. (2).(you'll find that it'll be less than 56.4 kJ/mol.)

2-determine $\Delta H_{ionization}$:

$\Delta H_{\text{ionization}} = -13.7 - \Delta H_{\text{neutralization}}$ Cal/mol.

Or $\Delta H_{\text{ionization}} = -56.4 - \Delta H_{\text{neutralization}}$ kJ/mol.

Experiment (4) Determination of the heat of dilution of sulfuric acid

- The heat of dilution is the heat liberated or absorbed when a solution of higher concentration is diluted to a solution of lower concentration.
- It depends on the initial & final concentrations
- The amount of heat evolved by dilution (Q_{dilution}) = $Q_{\text{aqueous solution}} + Q_{\text{calorimeter}}$

$$\mathbf{Q_{dilution} = (4.18)\ (30)\ \Delta t + (30)\ \Delta t}$$

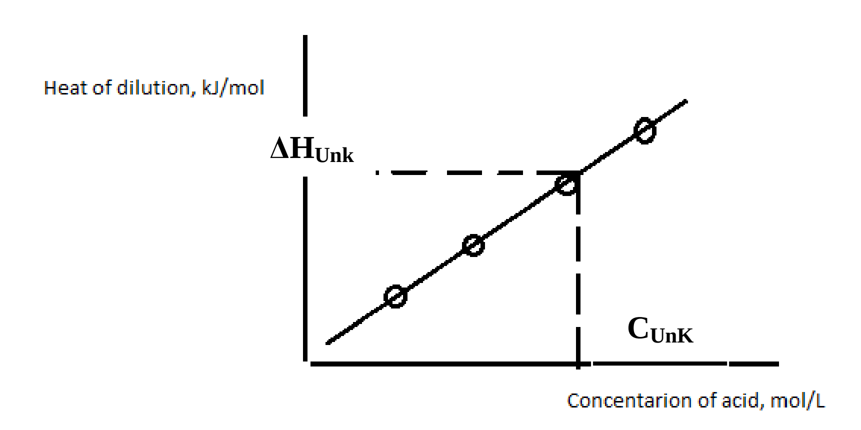
Procedure

1. In a clean & dry calorimeter, add 25 mL of distilled water& record the initial temperature (t_i)
2. Transfer 5 ml of 60 % H_2SO_4 , stir well & record the final temperature (t_f)
3. Repeat the above two steps for 70 %, 80 % & unknown H_2SO_4 concentration
4. Tabulate your results as follows:

% of H_2SO_4	Initial concentration of H_2SO_4 (mol/L)	Final concentration of H_2SO_4 (mol/L)	$n = M \times V_L$	$t_{initial}$	t_{final}	Δt	$\Delta H_{dilution} = Q_{dilution} / n$
60	11.27	1.88	1.88 X 0.03				

70	**13.14**	**2.19**	**2.19 X 0.03**				
80	**15.02**	**2.50**	**2.50 X 0.03**				
Unknown	**?**	**?**	**?**				

5. Plot a graph of $\Delta H_{dilution}$ vs. final concentration of H_2SO_4 & from it deduce the unknown concentration.



Experiment (5): Heat of solution of oxalic acid

*the equilibrium between a solid &its saturated solution :

Solid solute ⇆ dissolved solute

The equilibrium constant $k_s = \frac{[\text{dissolved solute}]}{[\text{solid solute}]}$, [solid solute] ≈1

$$Ks \propto [\text{dissolved solute}]$$

$$Ks \propto Cs$$

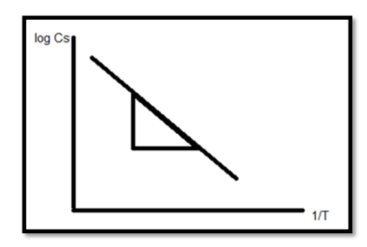
Where, Cs is the molal concentration of dissolved solute (mole of solute /1 kg of solvent)

*According to "van't hoff " isochore:

$$\frac{d \ln k_s}{d\,T} = \frac{\Delta H}{RT^2}$$

Where , ΔH: is the heat of solution which is the change in heat content when 1 mole of solute is dissolved in a large volume of saturated solution

By integration



$$\therefore \int d \ln Cs = \frac{\Delta H}{R} \int \frac{dT}{T^2}$$

$$\therefore \ln Cs = -\frac{\Delta H}{R}\frac{1}{T} + \text{contant}$$

$$since \int \frac{dT}{T^2} = -\frac{1}{T} + constant$$

$$\therefore \log Cs = -\frac{\Delta H}{2.303R}\frac{1}{T} + \text{constant}$$

$$\text{Slope} = \frac{-\Delta H}{2.303R}$$

procedure:

1 -Prepare a saturated oxalic acid solution in a large test tube (20 g of oxalic acid +70 ml of distilled water)

2 – Heat to~ 60°C for 5min ,then cool down to the desired temperature (40°C)& leave it for 20min. at 40c° to attain equilibrium

3 – Withdraw by a pipette 10 ml of the clear supernatant solution (clear)
into 100 ml-measuring flask &complete to the mark with distilled water (dilution)
*the pipette is plugged with a small cotton to prevent withdrawal of fine crystals with the solution
*the pipette must have the same temp .of the solution to prevent the precipitation of the dissolved solute into the pipette (as solubility ↓as temp.↓)
4 – Withdraw 10 ml of diluted acid solution &titrate it against 0.5N NaOH using ph.ph. indicator (end point is very faint pink)
5 – Repeat the above steps at 30°C &20°C

<u>In case of determining the heat of solution of benzoic acid the titration is carried out with the saturated acid solution without dilution</u>

<u>Calculations :</u>

At the end pint (e.p.) : $(MV)_{NaOH} = (MV)_{diluted\ oxalic\ acid}$

$\therefore M_{diluted\ oxalic\ acid} = \frac{(MV)_{NaOH}}{10}$

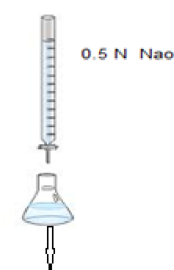
Then, to calculate $M_{oxalic\ acid\ before\ dilution}$

$(MV)_{oxalic\ acid\ before\ dilution} = (MV)_{oxalic\ acid\ after\ dilution}$

$\therefore M_{oxalic\ acid\ before\ dilution} = \frac{(MV)_{oxalic\ acid\ diluted}}{10}$

For very diluted solution molarity ≈ molality

$\therefore Cs = M_{oxalic\ acid\ before\ dilution}$



Tabulate your result as follows:

t/°C	$\frac{1}{T}/k^{-1}$	$V_{burette}$	Cs=0.5x $V_{burette}$	Log Cs
40				
30				
20				

Then ,plot log Cs vs. $\frac{1}{T}$ & from the slope ,calculate ΔH : ΔH = -(slope)(2.303)(R)

Chapter 6

Kinetic Chemistry 2

Chemical kinetics

Types of chemical reaction

Chemical reaction con be divided according to:

1- the phase of the reactants

a- Homogeneous Reaction Definition:

Homogeneous reactions are chemical reactions in which the reactants are in the same phase.

Examples:

$N_2(g)+3H_2(g) \longrightarrow 2NH_3(g)$

b- Heterogeneous Reaction Definition :

A heterogeneous reaction is *a chemical reaction* where the reactants are in different phases from each other.

Examples:

The reaction between acid and metal is a heterogeneous reaction.

$\mathbf{C_{(S)} + O_{2(g)} \longrightarrow CO_{2(g)}}$

2- Chemical reaction depending on the direction of the interaction:

a-Irreversible reaction:

are reactions where the reactants convert to products and where the products *can not* convert back to the reactants

$C_{(S)}+O_{2(g)} \longrightarrow CO_{2(g)}$

b-A reversible reactions:

are chemical reactions where the reactants form products that, in turn, react together to give the reactants back.

$H_{2(g)}+ I_{2(g)} \longleftrightarrow 2HI_{(g)}$

$N_{2(g)}+3H_{2(g)} \longleftrightarrow 2NH_{3(g)}$

*The main use of chemical kinetics is to measure the speed of a chemical reaction (the rate of the reaction) which is the rate by which reactants are consumed or products are produced .

For the reaction: reactants →products

$$\text{Rate} = -\frac{d[reactants]}{d(time)} = +\frac{d[products]}{d(time)}$$

[reactants]: reactants concentration

[products]: products concentration

the –ve sign means that [reactants] decreases with time

Therefore, the rate of reaction can be get by dividing the concentration on the time (moles/liter sec, moles/liter min, etc.).

***The rate law**

$$A+B \xrightarrow{C(catalyst)} products$$

the dependence of the rate on the concentration can be expressed as:

Rate $=k[A]^x [B]^y[C]$

$=k` [A]^x [B]^y$

(k : rate constant & x,y are the concentration terms of A,B respectively affecting the rate) (k` =k[C]) since the catalyst concentration is constant

***Factors affecting the rate of a chemical reaction:**

1 – the concentration of reactants

As [reactants]↑,the rate increases

2 – the temperature

As temp. ↑,the rate increases.

Usually reactions speed up when the temperature increases.

3 – the catalyst:

The presence of the catalyst enhances the reaction rate .

A catalyst is a substance that increases the rate of a reaction without being consumed in the overall reaction.

4 – the surface area:

As the surface area of reactants increases (smaller particle size) the rate is increased also, the reaction is faster by increasing the surface area of the catalyst .

The Law of Mass Action:

In a chemical reaction:

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D$$

$$\frac{[C]^c [D]^d}{[A]^a [B]^b} = K_{eq}$$

Examples

1. **Write the the equilibrium constant expression for the reaction equation:**

$NH_3 + HOAc = NH_4^+ + OAc^-$.

$[NH_4^+] [OAc^-]$

--------------------- = K (unitless constant)

$[NH_3]$ [HOAc]

***The reaction order**

The number of reactants molecules that participate in the rate-determining step (affecting the reaction rate)

Reaction Order = x+y

While ,the molecularity is the number of reactants molecules that participate in the reaction.

Consider the hydrolysis of ester to produce alcohol &acid

$CH_3COOCH_3+H_2O \underset{H}{\leftrightharpoons} CH_3COOH+CH_3OH$

Molecularity =2 (1ester +1H_2O)

While reaction Order =1 (1^{st} order reaction with respect ester)

Since, molecularity ≠ reaction Order

In this case ,the acid hydrolysis of ester is "pseudo first order reaction "

1^{st} order reaction

for the reaction:

	A →	products
t =0	a	0
after time=t	(a-x)	x

The initial concentration of the reactant A=a (t=0)

after time = t ,the concentration of the reactant is decreased by x = (a-x) & the concentration of the reactant is increased by x

*According to the rate law :

Rate = $-\frac{d[A]}{dt} = -\frac{d(a-x)}{dt}$ Or, Rate = $\frac{d[products]}{dt} = = \frac{dx}{dt}$

∴the reaction is 1^{st} order reaction with respect to A

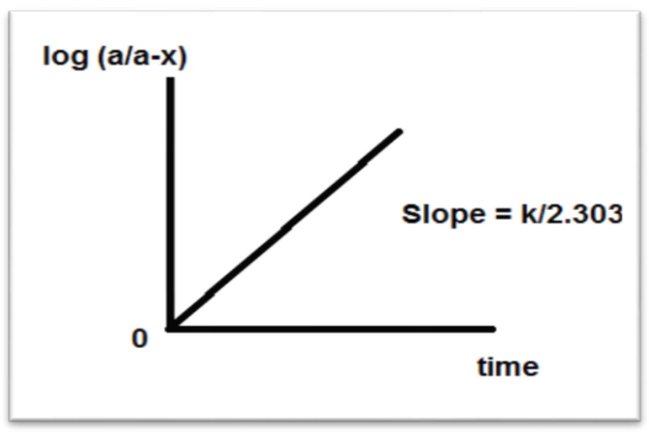
Rate = $\frac{dx}{dt}$ =k $(a-x)^1$ **differential form**

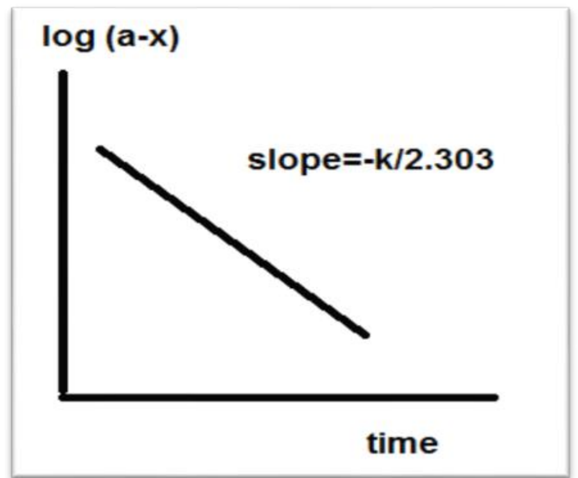
by integration: $\int\frac{dx}{(a-x)} = k\int dt$

$\therefore \ln\left(\frac{a}{a-x}\right) = kt$

k = $\frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$ **integral form**

Linear relationships





Unit of k for 1st order reaction: (time unit)$^{-1}$: sec^{-1},min^{-1} ,h^{-1},year $^{-1}$

Half –life time ($t_{1/2}$)

It's the time required for the reactants concentration to decrease to half of its initial value

i.e.	A	→	proclcts
t=0	a		zero
time=t	a-x		x
t=$t_{½}$	a/2		a/2

for 1^{s1} order reaction $t_{1/2} = \frac{2.303}{K} \log(2)$

$t_{1/2} = 0.693/k$

2nd order reaction

	A + B	→	products
t=0	a b		zero
time=t	a-x b-x		x

Consider the two reactants have the same initial concentration

	A + B	→	Products
t=o	a a		zero
time=t	a-x a-x		x

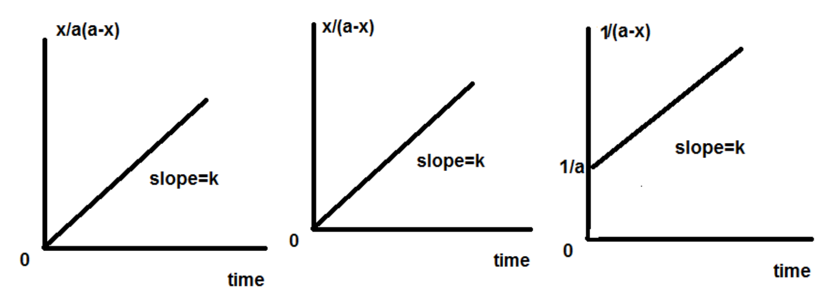
Rate = $\frac{dx}{dt} = k(a-x)^2$ **differential form**

by integration $\int \frac{dx}{(a-x)^2} = k \int dt$

$\therefore \frac{x}{a(a-x)} = kt$

$k = \frac{x}{ta(a-x)}$ **integral form**

Linear relationships



Unit of k for 2nd order reaction (concentration unit)$^{-1}$.(time unit)$^{-1}$

i.e. $(mol/L)^{-1} (min)^{-1}$, $mol^{-1} .min^{-1} .L$

Half-life time

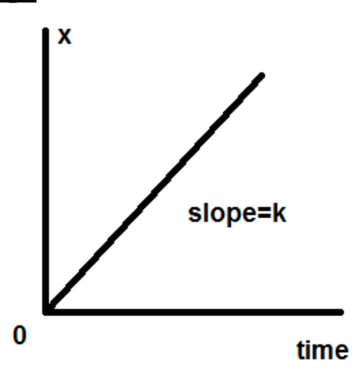
$t_{½} = \frac{1}{ka}$ (depends on the initial concentration of reactants)

zero –order reaction : the reaction rate is independent of the reactants concentration

Rate $= \frac{dx}{dt} = k$ **differential form**

$\therefore k = \frac{x}{t}$ **integral form**

Linear relationships



Unit of k for zero –order reaction. (concentration unit)(time unit)$^{-1}$
i.g (mol/L)(min)$^{-1}$,mol/L. min

Half- life time:

$$t_{½} = \frac{a}{2k}$$



References

1. J. Shriver and M. George " Experimental Physical Chemistry " University of Alabama, 2006

2. G. Mohanta and P. Manna " Physical Pharmacy Practical Text " , Pharma Med Press, 2006

3. P. Parasania " Practical Book of Physical Chemistry ", Suarashtara University, 2009



Table of Contents

